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HEAT RELEASE KINETICS

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ABSTRACT

The heat release rate in steady, flaming combustion is obtained from solid state thermal degradation kinetics using a simple models of polymer burning. Detailed thermal degradation chemistry is foregone in favor of a transient mass balance on the polymer, fuel gases, and solid char in the anaerobic pyrolysis zone. Closed-form, time-independent solutions for the scalar mass loss rate and char yield are obtained from the degradation kinetics which, in combination with the solid state heat transport provide the scaling relationship between material properties and steady burning rate.

FIRE BEHAVIOR OF COMBUSTIBLE SOLIDS

Once sustainable ignition has occurred, steady, one-dimensional burning of the thermally-thick polymer is assumed. Steady burning at a constant surface heat flux is treated as a stationary state by choosing a coordinate system which is fixed to the surface and moving at the recession velocity v as shown in Figure 1.
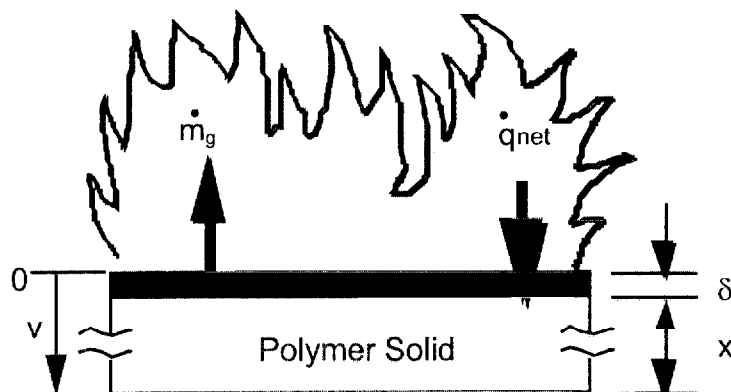

Figure 1. Geometry of Polymer Combustion Analysis

If there is no internal heat generation or absorption, the one-dimensional heat conduction equation applies

$$\rho c \frac{T}{t} - \rho c v \frac{T}{x} = \kappa \frac{^2 T}{x^2} \tag{1}$$

where T is the temperature at location x in the solid polymer of thermal conductivity, κ, density, ρ, and heat capacity, c; and v is the regression velocity of the burning surface. Under steady-state conditions, $dT(x)/dt = 0$ and the pyrolysis zone of constant thickness δ moves through the infinitely thick solid with a fixed temperature gradient so that Equation 1 becomes

$$\frac{d^2 T}{dx^2} + \frac{v}{\alpha} \frac{dT}{dx} = 0 \tag{2}$$

for steady burning of a material with a constant thermal diffusivity, $\alpha = \kappa/\rho c$. The solution for the temperature distribution is

$$T(x) = T_o + \left[\frac{\dot{q}_{net}}{\rho c v} - \frac{\Delta h_v}{c} \right] \exp\left[-\frac{v}{\alpha} x \right] \tag{3a}$$

or

$$T(x) - T_o = \left(T_p - T_o \right) \exp\left(-\frac{c \dot{q}_{net}}{\kappa h_g} x \right) \tag{3b}$$

for a steady recession velocity of the surface $x = 0$ at surface temperature $T(0) = T_s \ T_p$

$$v = \frac{1}{\rho} \frac{\dot{q}_{net}}{\left(c (T_p - T_o) + \Delta h_v \right)} = \frac{1}{\rho} \frac{\dot{q}_{net}}{h_g} \tag{4}$$

where $\dot{q}_{net}$ is the net surface heat flux, T_p is the peak mass loss (pyrolysis) temperature, and h_g is the heat of gasification per unit original mass of polymer[1]

$$h_g = c(T_p - T_o) + h_v. \tag{5}$$

Equation 3 is in qualitative agreement with experimental data[2] for the temperature gradient in steadily burning liquid pools if T_p is taken as the boiling temperature of the liquid fuel.

Conservation of mass for the control volume in which the virgin polymer of density ρ pyrolyzes to an inert or char fraction μ where μ = mass of char/original mass, gives

$$\rho v = \frac{\dot{m}_g}{1 - \mu} \tag{6}$$

where $\dot{m}_g$ is the mass loss rate of pyrolysis gases per unit surface area. Defining a heat of gasification per unit mass of volatiles

$$L_g = \frac{h_g}{1 - \mu} \tag{7}$$

and combining Equations 4, 6, and 7

$$\dot{m}_g = \frac{\dot{q}_{net}}{h_g/(1-\mu)} = \frac{\dot{q}_{net}}{L_g} \qquad (8)$$

The heat of gasification per unit mass of solid polymer h_g can be determined from the reciprocal slope of a plot of areal mass loss rate *versus* external heat flux if the char yield μ is measured after the test, since

$$\dot{m}_g = \frac{\dot{q}_{ext}}{L_g} - \left(\frac{\dot{q}_{flame} - \dot{q}_{cr}}{L_g}\right) \qquad (9)$$

Multiplying Equation 9 by the net heat of complete combustion of the volatile polymer decomposition products h_c^o and the gas phase combustion efficiency χ gives the usual result for the average heat release rate of a burning specimen[1],

$$\dot{q}_c = \chi h_c^o \dot{m}_g = \chi(1-\mu)\frac{h_c^o}{h_g}\dot{q}_{net} = \chi\frac{h_c^o}{L_g}\dot{q}_{net} \qquad (10)$$

In the following kinetic development of the fuel generation rate from thermal degradation reactions it will be useful to know the rate of temperature rise at the surface as the pyrolysis zone moves through the solid at constant velocity, v. From Equations 6 and 7 the effective heating rate at the surface is

$$\left.\frac{dT}{dt}\right|_{x=0} = v\left.\frac{dT}{dx}\right|_{x=0} = \frac{\dot{q}_{net}^2}{\kappa\rho c\left(T_p - T_o\right)}\left(1 + \frac{\Delta h_v}{h_g}\right) \qquad (11a)$$

where h_v is the heat of vaporization of the degradation products. Typically[3], h_v/h_g 0.1, so that to a good approximation the heating rate at the surface from Equation 11a is

$$\left.\frac{dT}{dt}\right|_{x=0} \approx \frac{1}{2}\frac{\dot{q}_{net}^2}{\kappa\rho c(T_p - T_o)} \approx \frac{\dot{q}_{net}^2}{\kappa\rho h_g} \qquad (11b)$$

According to Equation 11b the rate of surface temperature rise of a polymer with T_p 500°C (723 K) and a typical $\kappa\rho c = 5 \times 10^5$ W-s-m^{-4}-K^{-2} experiencing a 50 kW/m^2 net surface heat flux is dT/dt = 5 K/s.

FUEL GENERATION KINETICS

The first stage of thermal degradation at a burning surface produces primary volatiles (gas and tar) and possibly a primary char residue. If a primary char forms, further decomposition occurs by dehydrogenation to form the secondary gas (principally hydrogen) and a thermally stable secondary carbonaceous char as illustrated schematically in Figure 2.
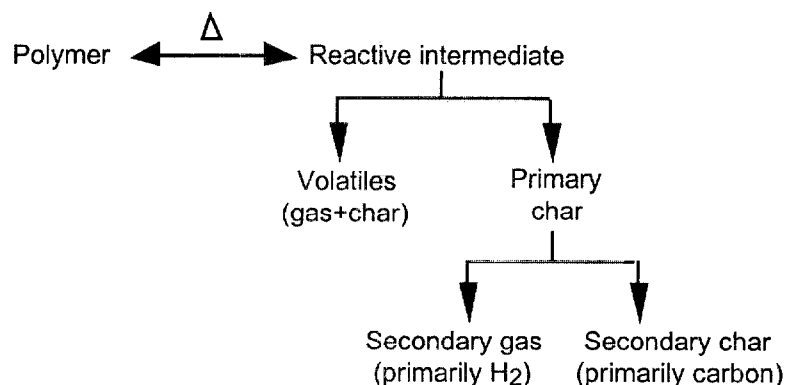
Figure 2. Generalized Thermal Degradation Mechanism of Polymers

A simple, solid-state fuel generation model has been derived[4] from Figure 2 with the following assumptions about the process of polymer thermal degradation as it occurs in fires:

1. A reactive intermediate I* is generated in the polymer dissociation (initiation) step which is in rapid dynamic equilibrium with the parent polymer, P, but is consumed in the process of gas and char formation such that its concentration never becomes appreciable and decreases slowly over time as the polymer is consumed. This is the stationary-state hypothesis.

2. For practical purposes, thermal decomposition can be treated as a single step process[5].

3. The thermal degradation environment in the pyrolysis zone of a burning solid polymer is non-oxidizing or anaerobic. Dissolved molecular oxygen and oxygen diffusion into the pyrolysis zone of the solid are considered negligible with respect to their effects on gas and char formation so that solid-state oxidation reactions can be neglected in the fuel generation model for polymers in fires.

Figure 3 shows data[3] for a variety of pure, unfilled polymers plotted as the char yield measured after flaming combustion in a fire calorimeter *versus* the char residue at 850-900°C for the same material after anaerobic pyrolysis. It is seen that the char yield of a material in a fire is essentially equal to its residual mass fraction after pyrolysis in an oxygen-free environment at temperatures representative of the char temperature in a fire. Although oxidative degradation products have been identified at the surface of noncharring olefinic polymers after flaming combustion [6,7] the close agreement between fire char yield and anaerobic pyrolysis residue in Figure 3 suggest that oxidation reactions are insignificant in the char formation process as it occurs in the pyrolysis zone of a burning polymer.
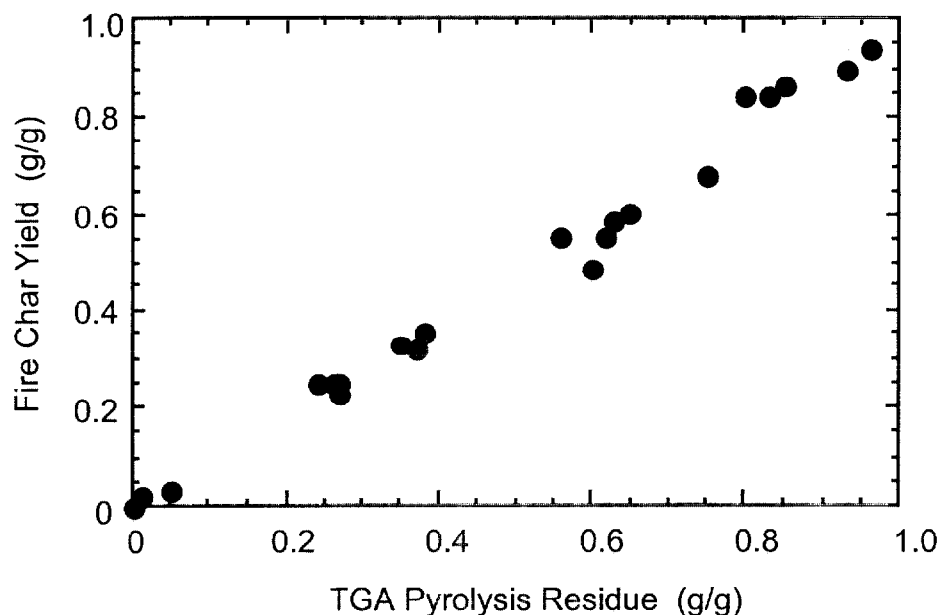
Figure 3. Fire Char Yield *versus* Anaerobic Pyrolysis Residue for a Variety of Polymers

The generalized combustion and pyrolysis scheme of Figure 2 in combination with assumptions 1–3 lead to the simplified kinetic model for polymer combustion shown in Figure 4.
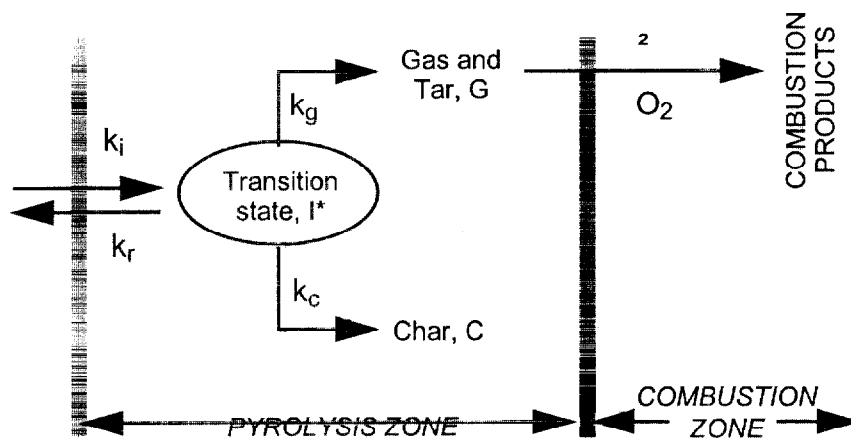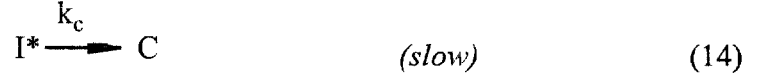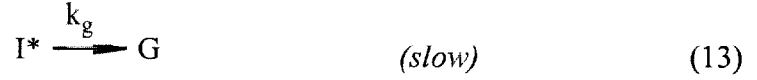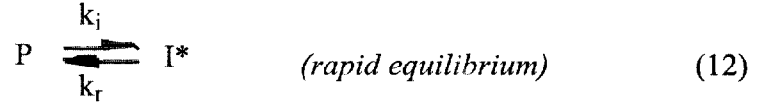

Figure 4. Thermal Degradation Model for Polymers in Fires

This simplified scheme reduces thermal degradation of polymer P to a single step involving parallel reactions of an active intermediate I* to form to gas G and char C. In Figure 5, k_i is the rate constant for initiation, and k_r, k_g, and k_c are the rate constants for termination by recombination (k_r), hydrogen transfer to gaseous species (k_g), and crosslinking to char (k_c), respectively. Neglecting solid-state oxidation the thermal decomposition reactions are

$$P \; \overset{k_i}{\underset{k_r}{\rightleftharpoons}} \; I^* \qquad \textit{(rapid equilibrium)} \qquad (12)$$

$$I^* \xrightarrow{k_g} G \qquad \textit{(slow)} \qquad (13)$$

$$I^* \xrightarrow{k_c} C \qquad \textit{(slow)} \qquad (14)$$

and the system of rate equations for the species at time, t, is

$$\frac{dP}{dt} = -k_i P + k_r I^* \qquad (15)$$

$$\frac{dI^*}{dt} = k_i P - \left(k_r + k_g + k_c\right) I^* \qquad (16)$$

$$\frac{dG}{dt} = k_g I^* \qquad (17)$$

$$\frac{dC}{dt} = k_c I^* \qquad (18)$$

According to the stationary-state hypothesis, $dI^*/dt \approx 0$ so that Equation 15 provides the useful result

$$I^* = \left[\frac{k_i}{k_r + k_g + k_c}\right] P = K P$$

where $K = k_i/(k_r + k_g + k_c)$ is the pseudo-equilibrium constant for the polymer dissociation reaction. The isothermal solution of Equations 17-20 is straightforward[4].

Solution of Equations 15-18 for $dI^*/dt \approx 0$ at a constant heating rate $\beta = dT/dt$, gives for the extent of polymer reaction at temperature T

$$\frac{M(T)}{M_0} = Y_c(T) + [1 - Y_c(T)] e^{-y} \qquad (19)$$

where M_0 is the initial mass,

$$y = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_a}{R\theta}\right) d\theta \approx \frac{ART^2}{\beta(E_a + 2RT)} \exp\left(-\frac{E_a}{RT}\right) = \frac{k_p RT^2}{\beta(E_a + 2RT)}$$

and

$$Y_c(T) = \frac{M(\infty)}{M_0} = \frac{k_c}{k_g + k_c}$$

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is the *equilibrium* residual mass fraction or char yield at temperature T in terms of the rate constants for gas k_g and char k_c formation. The overall rate constant for thermal degradation is

$$k_p = k_i - Kk_r = K(k_g + k_c) = A \exp\left(-\frac{E_a}{RT}\right) \qquad (20)$$

in terms of the global activation energy E_a and frequency factor A for pyrolysis. Differentiating Equation 19 twice with respect to time at constant heating rate gives an expression for the peak mass loss rate

$$\left.\frac{-1}{M_0}\frac{dM}{dt}\right|_{max} \approx (1-\mu)\frac{\beta E_a}{eRT_p^2} \qquad (21)$$

Multiplying Equation 21 by the heat of complete combustion of the volatile thermal degradation products h_c^o gives the time-independent (peak) kinetic heat release rate at constant heating rate β

$$\dot{Q}_c(W/kg) = -h_c^o \frac{\dot{M}_{max}}{M_0} \approx h_c^o \frac{\beta(1-\mu)E_a}{eRT_p^2} \qquad (22)$$

Substituting Equations 20 and 3 into Equation 10, it can be shown that the steady macroscopic heat release rate per unit area of burning surface for a pyrolysis zone thickness δ (see Figure 1) is[8]

$$q_c(W/m^2) = \chi h_c^o \langle \dot{m}_g \rangle = \chi h_c^o \int_0^\delta \rho_g k_p(x)\,dx = \chi\rho\delta\left(h_c^o\frac{\dot{M}_{max}}{M_0}\right) = \chi\rho\delta\dot{Q}_c \qquad (22)$$

from which the ratio of the macroscopic and kinetic heat release rates at comparable surface heating rates is

$$\frac{q_c}{Q_c} = \chi\rho\delta \qquad (23)$$

Thus, proportionality between the macroscopic heat release rate and the kinetic heat release rate depends on the product of the gas phase combustion efficiency χ, polymer density ρ, and pyrolysis zone thickness δ. The pyrolysis zone thickness can be estimated using the criteria that the mass loss rate falls to $1/e$ of the surface (x = 0) value at $1/e$ of the pyrolysis zone thickness x = δ/e. The result is[3,8]

$$\delta = \frac{\kappa}{\dot{q}_{net}}\frac{eRT_p^2}{E_a} \qquad (24)$$

For typical polymer values $T_p = 750$ K, $E_a = 200$ kJ/mol, and $\kappa(T_p)$ 0.2 W/m-K, Equation 24 predicts δ 0.3 mm at a net incident heat flux, $\dot{q}_{net} = 50$ kw/m^2, which is in agreement with estimates[2,9] δ 1 mm.

A rate-independent flammability parameter comprised only of material properties emerges from this analysis when the kinetic heat release rate $\dot{Q}_c$ (Equation 22) is normalized for heating rate

$$\eta_c \equiv \frac{\dot{Q}_c}{\beta} = \frac{h_c^o(1-\mu)E_a}{eRT_p^2} \tag{25}$$

The thermokinetic flammability parameter η_c has the units (J/g-K) and significance of a heat [release] capacity when the linear heating rate is β(K/s). Substituting the heat release capacity η_c (Equation 25), pyrolysis zone depth δ (Equation 24), and surface heating rate β (Equation 11) into Equation 22 recovers the steady heat release rate in flaming combustion (Equation 10) from the thermochemistry after cancellation of terms

$$\dot{q}_c = \chi\rho\delta\beta\eta_c = \chi\rho\left[\frac{\kappa}{\dot{q}_{net}}\frac{eRT_p^2}{E_a}\right]\left[\frac{\dot{q}_{net}^2}{\kappa\rho\,h_g}\right]\left[\frac{h_c^o(1-\mu)E_a}{eRT_p^2}\right] = \chi\frac{h_c^o}{L_g}\dot{q}_{net} \tag{26}$$

Obtaining the macroscopic heat release rate from the derived diffusion (β) thermokinetic (η_c) and coupling (δ) parameters shows that the present thermochemical treatment of steady burning is self-consistent.

ACKNOWLEDGEMENTS

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